

Asymptotic behavior of the electron density and the Kohn-Sham potential

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It is known that the asymptotic decay ($|\mathbf{r}| \rightarrow \infty$) of the electron density $n(\mathbf{r})$ outside a molecule is informative about its first ionization potential I_0 . Contrary to conventional wisdom, we demonstrate that this asymptotic decay may not be the same in every direction. When the highest occupied Kohn-Sham molecular orbital has a nodal plane, the decay $n(|\mathbf{r}_p| \rightarrow \infty)$ on that plane is informative about a higher vertical ionization potential I_i . The implications for density functional theory are manifold: the Kohn-Sham potential does not need to have an asymptotic constant shift on the plane as previously believed, provided that the second highest occupied orbital energy equals $-I_i$. The effective potential for $\sqrt{n(\mathbf{r})}$ may diverge asymptotically on the plane.

In Kohn-Sham (KS) density functional theory (DFT), which is perhaps the most widely used technique in electronic structure theory, ground-state properties are calculated via the KS system, consisting of non-interacting electrons moving in the local KS potential $v_s(\mathbf{r})$. In principle, the KS potential $v_s(\mathbf{r})$ ensures that the electron density $n(\mathbf{r})$ of the non-interacting KS system is the same as that of the physical, interacting system. Exact properties of $n(\mathbf{r})$ and $v_s(\mathbf{r})$ have played – and continue to play – a crucial role in constructing and improving approximations.

Both the (square root of the) density and the KS orbitals $\psi_k(\mathbf{r})$ obey Schrödinger-type equations,

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{eff}}(\mathbf{r})\right) \sqrt{n(\mathbf{r})} = -I_0 \sqrt{n(\mathbf{r})} \quad (1)$$

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r}) + v_{\text{Hxc}}(\mathbf{r})\right) \psi_k(\mathbf{r}) = \epsilon_k \psi_k(\mathbf{r}), \quad (2)$$

where $v_s = v_{\text{ext}} + v_{\text{Hxc}}$ and $I_0 = E_0^{N-1} - E_0^N$ is the first ionization potential, and $\sum_k |\psi_k(\mathbf{r})|^2 = n(\mathbf{r})$. Here the external potential $v_{\text{ext}}(\mathbf{r})$ is a nuclear potential going to zero at large distance like $-Z/r$ where Z is the total charge of all nuclei and r is the distance from the center of nuclear charge. In this case, according to Eqs. (1)-(2), the asymptotic ($r \rightarrow \infty$) decay of $\sqrt{n(\mathbf{r})}$ and $\psi_k(\mathbf{r})$ is $\sim e^{-\sqrt{2(I_0 + v_{\text{eff}}(\infty))}r}$ and $\sim e^{-\sqrt{2(-\epsilon_k + v_{\text{Hxc}}(\infty))}r}$ respectively. Both the effective potential $v_{\text{eff}}(\mathbf{r})$ for $\sqrt{n(\mathbf{r})}$ and v_s (i.e. the Hartree-exchange-correlation potential $v_{\text{Hxc}}(\mathbf{r})$) have been thought to go to 0 asymptotically. In the KS case there is, with the local KS potential, no coupling of the eigenvalue equations, as there is in the case of Hartree-Fock (HF) [1]. Therefore the density decays as the square of the highest-occupied molecular orbital (HOMO), leading to the identification $I_0 = -\epsilon_H$ [2, 3]. In case the KS HOMO has a nodal plane (HNP), a very straightforward argument was given by Wu *et al.* [4] that the KS potential should go to a *negative* constant for asymptotic points $r_p \rightarrow \infty$ in that plane. The KS density in that plane is governed by the HOMO–1, assuming HOMO–1 does not have the same nodal plane. Wu *et al.* [4] made the common

assumption that the exact interacting density has the same asymptotic behavior everywhere, and they deduced that the decay of the HOMO–1 in the HNP must be equal to the decay of the total density, implying $-\sqrt{2(-\epsilon_{H-1} + v_{\text{Hxc}}(r_p \rightarrow \infty))}r_p = -\sqrt{2I_0}r_p$, so that $v_{\text{Hxc}}(r_p \rightarrow \infty)$ should tend to the *negative* constant $I_0 + \epsilon_{H-1} = -(\epsilon_H - \epsilon_{H-1})$. On the other hand, it had earlier been argued, and numerical evidence had been provided, that the optimized effective potential method for the exact exchange model of Kohn-Sham (xOEP) leads to an asymptotic constant in the HNP, but *positive* [5–8]. Since it was pointed out that this behavior of the Kohn-Sham potential has a significant effect on the orbital energies of particularly the higher lying unoccupied orbitals, with large consequences for the excitation energies calculated with time-dependent DFT [5, 6], the matter has practical importance.

In this Letter we show that: (i) the asymptotic decay of the exact interacting density may be different in different directions: if there is a KS HOMO nodal plane, the decay $n(|\mathbf{r}_p| \rightarrow \infty)$ in that plane will be different (faster) than the decay outside the plane. We support our proof with results from a simple interacting model that fully captures the essence of the problem and is analytically solvable; (ii) the potential $v_{\text{eff}}(\mathbf{r})$ of Eq. (1), while normally going to zero asymptotically, exhibits a different asymptotic behavior in directions where the density decays differently: in the KS HNP it can tend asymptotically to a constant or even to infinity. We then give arguments that: (iii) the KS potential can still go everywhere asymptotically to zero, provided that, if there is a HNP, the KS orbital energy of the HOMO–1 is equal to the second vertical ionization potential, $\epsilon_{H-1} = -I_1$.

Asymptotic behavior of the exact density – Although it is commonly assumed that the exact density decays everywhere in the same way, it should be recognized that this is not always true. First of all, it can be easily shown for a noninteracting electron system (and also for the Hartree-Fock approximation – see below), that if there is a nodal plane in the HOMO, the density decays differently in that plane. For the exact density of an in-

interacting system, where a configuration mixing will involve many configurations, the matter is more subtle. To study the density decay in the general interacting case, we express the exact N -electron wavefunction Ψ_0^N and the exact density in terms of the Dyson orbitals $d_i(\mathbf{x})$,

$$\begin{aligned}\Psi_0^N &= N^{-1/2} \sum_i d_i(\mathbf{x}) \Psi_i^{N-1}(2 \cdots N), \\ d_i(\mathbf{x}) &= \sqrt{N} \int \Psi_i^{N-1}(2 \cdots N)^* \Psi_0^N(\mathbf{x}, 2 \cdots N) d2 \cdots dN, \\ n(\mathbf{x}) &= \sum_{i=0}^{\infty} |d_i(\mathbf{x})|^2,\end{aligned}\quad (3)$$

where the Ψ_i^{N-1} are the exact (ion) $N-1$ states and $\mathbf{x} = \mathbf{r}, s$. The sum over i goes over both the spin- \uparrow and spin- \downarrow Dyson orbitals. If e.g. $\mathbf{x} = (\mathbf{r}, s = \uparrow)$ then only the spin- \uparrow Dyson orbitals are nonzero at \mathbf{x} and contribute to $n(\mathbf{x}) = n(\mathbf{r}, \uparrow) = (1/2)n(\mathbf{r})$ in closed shell systems). Each state of the ion is associated with a one-particle wavefunction, its Dyson orbital. These orbitals constitute a nonorthogonal nonnormal, in general linearly dependent set. We define the conditional amplitude $\Phi(2 \cdots N; \mathbf{x})$ and associated quantities,

$$\begin{aligned}\Phi(2 \cdots N; \mathbf{x}) &= \frac{\Psi_0^N(\mathbf{x}, 2 \cdots N)}{\sqrt{n(\mathbf{x})/N}}, \\ n^{cond}(\mathbf{x}_2 | \mathbf{x}) &= (N-1) \int |\Phi(2 \cdots N | \mathbf{x})|^2 d3 \cdots dN, \\ v^{cond}(\mathbf{x}) &= \int \frac{n^{cond}(\mathbf{x}_2 | \mathbf{x})}{|\mathbf{r} - \mathbf{r}_2|} d\mathbf{x}_2.\end{aligned}\quad (4)$$

$\Phi(2 \cdots N; \mathbf{x})$ is a normalized $N-1$ electron wavefunction depending parametrically on the position \mathbf{x} . Its square describes the probability distribution of electrons at positions $2 \cdots N$ when one electron is known to be at \mathbf{x} . Its associated one-electron density $n^{cond}(\mathbf{x}_2 | \mathbf{x})$ is the density of the other electrons at position \mathbf{x}_2 when one electron is at \mathbf{x} , which is the normal one-electron density $n(\mathbf{x}_2)$ plus the full exchange-correlation hole surrounding position \mathbf{x} . Projecting the Schrödinger equation $\hat{H}^N \Psi_0^N = E_0^N \Psi_0^N$ against $\Psi_i^{N-1}(2 \cdots N)$ and using the expansion of Eq. (3) one obtains the usual equations for the Dyson orbitals,

$$\left(-\frac{1}{2}\nabla^2 + v_{\text{ext}}(\mathbf{r})\right) d_i(\mathbf{x}) + \sum_{k=0}^{\infty} X_{ik}(\mathbf{x}) d_k(\mathbf{x}) = -I_i d_i(\mathbf{x}). \quad (5)$$

Katriel and Davidson (KD) [9] pointed out that, due to the coupling integrals $X_{ik}(\mathbf{x}) \equiv \langle \Psi_i^{N-1} | \sum_{j>1} |\mathbf{r}_j - \mathbf{r}|^{-1} | \Psi_k^{N-1} \rangle_{2..N}$, the exponential decay of the coupled Dyson orbitals will be the same. This was demonstrated by Handy *et al.* [1] for the analogous case of coupling of the Hartree-Fock orbitals by the exchange term. The first Dyson orbital d_0 will have exponential decay $\sim e^{-\sqrt{2I_0} r}$ multiplied by a factor r^β with $\beta = Z - N + 1$, due to the $-Z/r$ decay of v_{ext} and the $(N-1)/r$ decay of the coupling term. KD find

that higher Dyson orbitals which have nonzero X_{i0} with the first Dyson orbital will have decay $r^{\beta-L^*} e^{-\sqrt{2I_0} r}$ with $L^* \geq 2$. Dyson orbitals that are not connected to d_0 will have different exponential decay, governed by the eigenvalue of the first orbital in such a connected set (which is disjunct from other sets). Considering the expansion of the density in Dyson orbitals in Eq. (3), KD have noted that, if the density decays for $|\mathbf{r}| \rightarrow \infty$ as the most slowly decaying term $|d_0(\mathbf{x})|^2$, its exponential decay would be $\sim e^{-2\sqrt{2I_0} r}$. Levy, Perdew and Sahni [3] proved this exponential decay in a different way, thereby proving that the leading term and not the infinite summation of Eq. (3) determines the density decay. The result $n(|\mathbf{r}| \rightarrow \infty) \sim |d_0(\mathbf{r})|^2 \sim e^{-2\sqrt{2I_0} r}$ is considered well established.

This picture changes if the KS HOMO has a nodal plane. The common thinking is that still the interacting density decays everywhere in the same way due to correlation effects [4]. Instead, by analyzing the Dyson orbitals we can see that a KS HNP also signifies special behavior of the interacting density. A nodal plane is typically due to antisymmetry with respect to a symmetry plane (consider, e.g., ethylene or benzene [5, 7]), but a HOMO nodal surface can occur also in more general situations. In the case of a symmetry plane, the exact interacting states of the molecule are either symmetric or antisymmetric with respect to the plane. For example, the ground state wavefunction corresponding to a closed shell configuration is totally symmetric with respect to that plane, while the first ion state will be antisymmetric (the KS first ion state surely will be so, and we will only consider the case that the same holds for the exact ion state). For points \mathbf{r}_p in the HNP the conditional amplitude $\Phi(2 \cdots N | \mathbf{x}_p)$ will be symmetric with respect to the plane. Therefore, the matrix element $\langle \Psi_0^{N-1} | \Phi(2 \cdots N | \mathbf{x}_p) \rangle_{2..N}$ will vanish, so that the first Dyson orbital is zero in the plane:

$$d_0(\mathbf{x}_p) = \sqrt{n(\mathbf{x}_p)} \langle \Psi_0^{N-1} | \Phi(2 \cdots N | \mathbf{x}_p) \rangle_{2..N} = 0 \quad (6)$$

When we consider the asymptotic behavior of higher Dyson orbitals, it is clear that with $d_0(\mathbf{x}_p) = 0$, the coupling to d_0 in Eq. (5) for points in the HNP will be zero for any higher Dyson orbital $d_{i>0}$. Therefore the decay in the HNP of those higher Dyson orbitals is not governed by d_0 . We then turn to $d_1(\mathbf{x}_p)$. If the corresponding excited ion state Ψ_1^{N-1} has the same symmetry with respect to the HNP as Ψ_0^N , this orbital will not be zero in the plane. It will decay in the plane like $e^{-\sqrt{2I_1} r_p}$, since in the eigenvalue equation (5) all the terms except those from ∇^2 can be neglected in the asymptotic region compared to I_1 . All higher Dyson orbitals that are connected to d_1 in the HNP will decay similarly. According to Eq. (3) the density will, for points in the HNP, decay as $|d_1(\mathbf{x}_p)|^2 \sim e^{-2\sqrt{2I_1} r_p}$, barring again, as for other directions, fortuitous cancellation of this behavior by the infinite summation. As an addendum to the results of Ref. [1], it may be shown in the same way that in

the HNP of a HF atom the other orbitals decay like the HOMO-1. We conclude that the *exact* density will have a different decay in the HNP than in general directions. We can prove this if the HNP is a symmetry plane, but we expect similar behavior to occur generally in case of an asymptotic nodal surface of the HOMO.

As this result goes against the current belief, we support it with a simple *fully interacting* case that can be solved analytically and captures the mathematical essence of the problem. Consider two spinless interacting electrons (with standard Coulomb $1/r$ interaction) in an external parabolic potential $v_{\text{ext}}(\mathbf{r}) = \frac{1}{2}\omega^2 r^2$. As well known, the corresponding hamiltonian is separable into center-of-mass $\mathbf{R} = \frac{1}{2}(\mathbf{r}_1 + \mathbf{r}_2)$ and relative $\mathbf{r}_{12} = \mathbf{r}_2 - \mathbf{r}_1$ coordinates, so that its exact wavefunction reads $\Psi_0^N(\mathbf{r}_1, \mathbf{r}_2) = \xi(\mathbf{R})\phi(\mathbf{r}_{12})$. With spinless electrons, the spatial wavefunction must satisfy $\Psi_0^N(\mathbf{r}_1, \mathbf{r}_2) = -\Psi_0^N(\mathbf{r}_2, \mathbf{r}_1)$, which implies that the ground state corresponds to the $\ell_{12} = 1$ spherical harmonic for the relative vector \mathbf{r}_{12} . We have then 3 degenerate ground-state wavefunctions, and we choose one of them by fixing $m_{12} = 0$: this way, we obtain an interacting density with a symmetry plane like the one encountered in molecules. With $v_{\text{ext}}(\mathbf{r}) = \frac{1}{2}\omega^2 r^2$, the way the ionization-energy information is embodied into the asymptotic of the density is obviously different than the molecular case: we have that $n(|\mathbf{r}| \rightarrow \infty) \sim r^{2q}e^{-\omega r^2}$, with $E_0^N - E_0^{N-1} = \omega(\frac{3}{2} + q)$, where $q \in \mathbb{R}$. The values of ω for which q is integer correspond to analytical solutions of the interacting $N = 2$ hamiltonian [10]. For $\ell_{12} = 1$, $\omega = \frac{1}{4}$ is one of those. We find that the corresponding interacting density decays as $n(|\mathbf{r}| \rightarrow \infty) \sim r^4 e^{-\omega r^2}$ everywhere except on the $z = 0$ plane, where it decays as $\sim r^2 e^{-\omega r^2}$, thus carrying a different ionization-energy information. This can be further confirmed by looking at the corresponding effective potential $v_{\text{eff}}(\mathbf{r})$. In fact, as it was pointed out by LPS [3], Eq. (1) is valid for any binding $v_{\text{ext}}(\mathbf{r})$, with $v_{\text{eff}}(\mathbf{r})$ expected to go to zero asymptotically everywhere (it is only the Coulombic nature of the electron-electron repulsion that matters for v_{eff}). Using our analytical density we have calculated by inversion $v_{\text{eff}}(\mathbf{r}) = \frac{\nabla^2 \sqrt{n(\mathbf{r})}}{2\sqrt{n(\mathbf{r})}} - v_{\text{ext}}(\mathbf{r}) - I_0$. The results are shown in Fig. 1: we clearly see that $v_{\text{eff}}(\mathbf{r})$ goes to zero asymptotically everywhere except on the plane $z = 0$. In the following we analyze in general the behavior of $v_{\text{eff}}(\mathbf{r})$ close to the HNP.

The effective potential for \sqrt{n} – The potential $v_{\text{eff}}(\mathbf{r})$ of Eq. (1) can be written in the form [3, 11]

$$\begin{aligned} v_{\text{eff}}(\mathbf{x}) &= v^{\text{cond}}(\mathbf{x}) + \frac{1}{2} \langle \nabla_{\mathbf{x}} \Phi(2 \cdots N | \mathbf{x}) | \nabla_{\mathbf{x}} \Phi(2 \cdots N | \mathbf{x}) \rangle \\ &+ \langle \Phi(2 \cdots N | \mathbf{x}) | \hat{H}^{N-1} - E_0^{N-1} | \Phi(2 \cdots N | \mathbf{x}) \rangle \\ &\equiv v^{\text{cond}}(\mathbf{x}) + v^{\text{kin}}(\mathbf{x}) + v^{N-1}(\mathbf{x}). \end{aligned} \quad (7)$$

LPS [3] stressed that each term in Eq. (7) is everywhere nonnegative and should tend to zero asymptotically. In fact, $v^{\text{cond}}(\mathbf{x})$ [see Eq. (4)], being the repulsive Coulomb

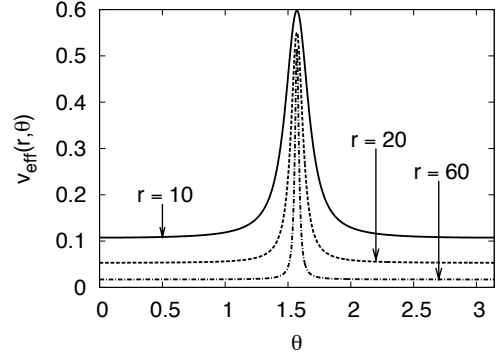


FIG. 1: The effective potential $v_{\text{eff}}(\mathbf{r})$ for $\sqrt{n(\mathbf{r})}$ in the case of the exactly solvable model described in the text, for larger and larger r as a function of $\theta = \arccos(\frac{z}{r})$.

potential of a localized charge distribution of $(N - 1)$ electrons, decays like $(N - 1)/r$. The third term of v_{eff} , v^{N-1} , is positive since in general Φ will not be the ground state wavefunction of the ion, so its expectation value will be larger than E_0^{N-1} . When $\mathbf{r} \rightarrow \infty$ it has been inferred that the conditional amplitude collapses to the ion ground state [9] (when $s = \uparrow$ then Φ will collapse to the $M_S = -1/2$ state of the doublet ion), so that $v^{N-1}(|\mathbf{r}| \rightarrow \infty) \rightarrow 0$. The second term, v^{kin} , is manifestly positive and is expected to go to zero asymptotically since the derivative of Φ with respect to \mathbf{r} when the reference electron is very far becomes zero (Φ remains constant – the ion ground state – under small change of \mathbf{r} at ∞).

LPS [3] and KD [9] carefully note that the above results do not hold if Ψ_0^{N-1} is not “accessible” because $d_0(\mathbf{x}) \equiv 0$ for reasons of *spin* symmetry. However, for points \mathbf{r}_p in the HNP $d_0(\mathbf{x}_p) = 0$ because of *spatial* symmetry. By expanding the conditional amplitude $\Phi(2 \cdots N | \mathbf{x})$ in terms of the exact $N - 1$ states,

$$\Phi(2 \cdots N | \mathbf{x}) = \sum_{i=0}^{\infty} \frac{d_i(\mathbf{x})}{\sqrt{n(\mathbf{x})}} \Psi_i^{N-1}(2 \cdots N), \quad (8)$$

we see that, since on the HNP $d_0 = 0$ and $n(|\mathbf{r}_p| \rightarrow \infty) \sim |d_1(\mathbf{x}_p)|^2$, on the plane the conditional amplitude tends asymptotically to the first-excited ion state, $\Phi \rightarrow \Psi_1^{N-1}$, implying that

$$v^{N-1}(|\mathbf{r}_p| \rightarrow \infty) = E_1^{N-1} - E_0^{N-1} = I_1 - I_0. \quad (9)$$

This is a *positive* constant appearing in the asymptotics of v_{eff} only on the HNP. But this is not the end of the story: the second term in Eq. (7), v^{kin} , can also be non zero at infinity: when crossing the HNP, the asymptotic conditional amplitude changes from Ψ_0^{N-1} to Ψ_1^{N-1} , so that the \mathbf{r} -derivative of Φ perpendicular to the plane can be nonzero on the HNP also when $|\mathbf{r}| \rightarrow \infty$. Its actual value depends on how $d_0(\mathbf{r} \rightarrow \mathbf{r}_p)$ goes to zero when approaching the nodal plane. For example, if we make the simple assumption that asymptotically, in spherical

coordinates, $d_0 \sim f(\cos \theta)e^{-\sqrt{2I_0}r}$ with $f(0) = 0$, and $d_1 \sim e^{-\sqrt{2I_1}r}$, by writing v^{kin} in the form [11–13]

$$v^{kin}(\mathbf{r}) = \sum_{i=1}^{\infty} \frac{|\nabla d_i(\mathbf{x})|^2}{n(\mathbf{r})} - \frac{|\nabla n(\mathbf{r})|^2}{8n(\mathbf{r})^2}, \quad (10)$$

it is easy to see that

$$v^{kin}(r_p \rightarrow \infty) \rightarrow \frac{1}{2} \frac{f'(0)^2}{r^2} e^{2(\sqrt{2I_1} - \sqrt{2I_0})r}, \quad (11)$$

showing that v^{kin} can go asymptotically to infinity on the HNP if $f'(0) \neq 0$ (as, e.g., in the case of π orbitals). A simple illustration of this fact can be obtained by calculating analytically the potential $v_{\text{eff}}(\mathbf{r})$ corresponding to the non-interacting density of 3 electrons in the configuration $1s^2 2p_z^1$ in the external potential $v_{\text{ext}} = -\frac{1}{r}$. There, we can clearly see that v_{eff} goes to zero asymptotically everywhere except on the plane $z = 0$, where it goes to infinity, as predicted by Eq. (11). This asymptotic diverging behavior of v_{eff} on the plane is perfectly compatible with an analytical, well-behaved density. The key point is that when we project Eq. (1) on the plane, we have to take into account also $\nabla^2 \sqrt{n}$ in the direction perpendicular to the plane. Usually, this term is zero when $r \rightarrow \infty$, but when there is a HNP this is not the case. In the exact interacting case of Fig. 1 we have, on the plane, $v^{kin}(\infty) = \text{const.}$, and we have verified analytically that $v_{\text{eff}}(r_p \rightarrow \infty) = I_1 - I_0 + v^{kin}(\infty)$.

The Kohn-Sham potential – What happens to the KS potential for $|\mathbf{r}_p| \rightarrow \infty$? We have seen that the argument of Ref. 4 for a negative constant has disappeared since the exact density has a different decay in the HNP than elsewhere. Since the KS density in the HNP is dominated by the HOMO-1, the requirement that the KS system gives the exact density implies that, on the plane, $\psi_{H-1}(r_p \rightarrow \infty) \rightarrow e^{-\sqrt{2I_1}r}$. If v_s goes to zero asymptotically everywhere, also on the plane, this would imply $\epsilon_{H-1} = -I_1$. The results of Refs. [5, 6] for a positive

constant are for the exact-exchange model, and do not imply that it also exists for the full KS potential [14, 15]. Conversely, it is hard to prove that a positive asymptotic constant C does not exist for v_s , since it would be compatible with the $e^{-\sqrt{2I_1}r}$ decay of the HOMO-1 if $\epsilon_{H-1} = -I_1 + C$ (with $0 < C < I_1 - I_0$). It is interesting to observe that the few accurate (but not exact) calculations that are available for the KS orbital energies [13, 16] suggest $\epsilon_{H-1} = -I_1$ and thus $C = 0$, but the verification is not very accurate. The KS energies are only obtained to ~ 0.05 eV accuracy, and the agreement of the first few upper valence orbital energies with the first exact primary ionization energies is of the order of ~ 0.1 eV anyway [13]. The calculations of the “exact” orbital energies use KS potentials that reproduce accurate CI densities. There is no indication that the KS potential, which uniquely corresponds to the CI density, exhibits any tendency towards a constant C at infinity in the HNP. However, such features in the KS potential are extremely difficult to obtain with good numerical precision. In any case, the order of magnitude of C obtained in the exact-exchange model [5, 6] cannot apply to v_s in view of the accuracy within which $\epsilon_{H-1} = -I_1$ for the available data.

Conclusions – We have proved that the exact interacting density does not necessarily have a uniform asymptotic decay; it carries different ionization-energy information in directions where the KS HOMO has a nodal plane. We have investigated the implications for DFT. The effective potential for \sqrt{n} will in general go to a constant in the HNP, or even diverge asymptotically. Our results strongly suggest that the exact KS $\epsilon_{H-1} = -I_1$ and that the exact v_s uniformly tends to zero asymptotically.

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